

## METASTABLE PHASE RELATIONS IN THE SYSTEM $\text{CaO-Al}_2\text{O}_3\text{-MgO-TiO}_2$ : APPLICATION TO Ca- AND Al-RICH INCLUSIONS

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**Introduction:** High temperature phases such as corundum, hibonite, grossite, and perovskite are among the earliest phases that condensed in the early solar nebula. Recent work has shown that defect-structured phases occur in some ultrarefractory inclusions as metastable, possibly more kinetically-favored alternatives to the thermodynamically predicted stable phase assemblages [1-4]. For example, Han et al. have shown that non-stoichiometry in hibonite is accommodated by extra “spinel” blocks in the structure instead of the equilibrium assemblages hibonite+corundum or hibonite+spinel. To explore these relations, we have conducted a series of experiments in the system  $\text{CaO-Al}_2\text{O}_3\text{-MgO-TiO}_2$ . Here we discuss the compositions and mineralogy of the experimental samples and how they relate to phases in refractory inclusions with a focus on perovskite and spinel.

**Methods:** For the series of annealing studies, a  $\text{CaO-Al}_2\text{O}_3$  eutectic melt is allowed to react with a pure alumina crucible at 1,530°C for either 4 hours or 5 days, followed by quenching in air. Later experiments were similar except that additions of 5 wt% MgO, and  $\text{CaTiO}_3$  were used to explore the effect of minor elements on the phase assemblages. The experimental conditions resulted in reaction zones ~100-300  $\mu\text{m}$  wide consisting of a hibonite layer immediately adjacent to the corundum, followed by a grossite layer, and finally krotite with residual quenched melt. For the experiments with Mg, spinel is distributed in all layers but is mainly concentrated in the krotite layer. In the Ti-bearing experiments, perovskite precipitated in association with the krotite and residual melt. In addition to the experiments, we also analyzed perovskite grains in the FUN inclusion SHAL [5] and a large compact type A CAI from Allende. The experiments and refractory inclusions were analyzed using a JEOL 7600F SEM and quantitative analyses were obtained using the JEOL 8530F field-emission electron microprobe.

**Results and Discussion:** We have previously reported the results on hibonite non-stoichiometry and metastability in this system [3-5] and showed that defect-structured hibonite forms in place of stoichiometric hibonite in high-temperature, Mg-bearing gas and melts. In all of our experiments, grossite and krotite are stoichiometric and did not incorporate Mg or Ti in solid solution.

In the Mg-bearing experimental samples, spinels with anomalous, Al-enriched non-stoichiometries occur in contact with corundum, hibonite and grossite. The spinel compositions represent a solid solution between  $\text{MgAl}_2\text{O}_4$  and  $\text{Al}_{8/3}\text{O}_4$  with up to a 30 mol% excess of the Al-spinel component, whereas the euhedral spinels in contact with krotite and residual melt in the same experiment are stoichiometric  $\text{MgAl}_2\text{O}_4$ . Further annealing of the experiments results in the conversion of the non-stoichiometric aluminous spinel to stoichiometric spinel. We have observed that the formation of aluminous spinel in the experimental runs suppresses grossite formation [3].

In the Ti-bearing experiments, we produced aluminous perovskite along the join  $\text{CaTiO}_3\text{-CaAlO}_{2.5}$  with up to 10 wt.%  $\text{Al}_2\text{O}_3$ , in contact with krotite and residual melt. The incorporation of Al in perovskite is accompanied by the formation of O vacancies. Phase equilibria studies show the maximum Al content in perovskite solid solutions gives a composition of  $\text{CaTi}_{0.75}\text{Al}_{0.25}\text{O}_{2.75}$  [6], and is possibly limited by Al-avoidance on the octahedral sites. We have observed aluminous perovskites in refractory inclusions, including SHAL, a coarse-grained hibonite-perovskite-rich FUN inclusion from Allende, and a spinel-hibonite (SHIB) inclusion from the Paris meteorite [7]. In SHAL and the SHIB, the perovskites contain up to ~3 wt.%  $\text{Al}_2\text{O}_3$ , but show no detectable Mg. Transmission electron microscope studies show that the Al-perovskites in both inclusions are homogeneous with no Al-bearing exsolution phases or inclusions. We do not observe any superstructures that arise from O vacancy ordering.

We also observed Al-perovskite as inclusions within gehlenite in a large compact type A CAI from Allende with similar Al contents as the perovskite in SHAL. A paqueite-like phase also occurs as inclusions in the gehlenite, and one hypothesis we are exploring is the possibility that the aluminous perovskite forms as a result of paqueite breakdown into gehlenite+Al-perovskite on cooling.

**Conclusions:** The presence of metastable phases such as non-stoichiometric defect-structured hibonite and aluminous perovskite in refractory inclusions instead of stable assemblages suggests that kinetic factors tied to cooling rates for either direct nebular condensates or very refractory melts are controlling their formation.

**References:** [1] Keller, L. P. (1991) *AGU* 72:141. [2] Han J. et al. (2017) *48th LPSC*, #2895. [3] Han J. et al. (2016) *47th LPSC*, #2848. [4] Han J. et al. (2016) *79th MetSoc*, #6534. [5] Keller, L. P. et al. (2012) *75th MetSoc*, #5313. [6] Imlach, J. A. and Glasser, F. A. (1968) *Trans. Brit. Ceram. Soc.* 67, 581. [7] Han, J. et al. (2017) this volume.